Claims

1. A process for the hydroformylation of compounds containing at least one ethylenically unsaturated double bond by reaction with carbon monoxide and hydrogen in at least one reaction zone in the presence of a catalytically active fluid which comprises a dissolved metal complex of a metal of transition group VIII of the Periodic Table of the Elements with at least one phosphoramidite compound as ligand, wherein the fluid is brought into contact with a base.

2. A process according to claim 1, wherein

   a) the ethylenically unsaturated compound(s) and carbon monoxide and hydrogen are fed into the reaction zone(s) and are reacted in the presence of the catalytically active fluid,

   b) an output is taken from the reaction zone and is subjected to a fractionation to give a fraction consisting essentially of the hydroformylation product and a fraction comprising the catalytically active fluid in which the by-products of the hydroformylation which have boiling points higher than that of the hydroformylation product are present and the metal complex is dissolved, and

   c) the catalytically active fluid is, if appropriate after separating off at least part of the by-products having boiling points higher than that of the hydroformylation product, recirculated to the reaction zone.

3. A process according to any of the preceding claims, wherein the base is selected from among bases soluble in the catalytically active fluid, bases immobilized on a solid phase and combinations thereof.

4. A process according to any of the preceding claims, wherein the base is selected from among basic nitrogen compounds.

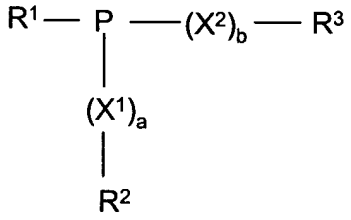
5. A process according to any of the preceding claims, wherein at least one base which is soluble in the catalytic fluid is used and a molar ratio of base to phosphoramidite compound of from 0.01:1 to 5:1, preferably from 0.1:1 to 1.5:1, is maintained in the reaction zone.

6. A process according to any of the preceding claims, wherein a combination of at least one base soluble in the catalytic fluid and at least one base immobilized on a solid phase is used and the immobilized bases are capable of at least partly liberating the soluble bases from the acid-base adducts obtained by reaction of the soluble bases with acids.

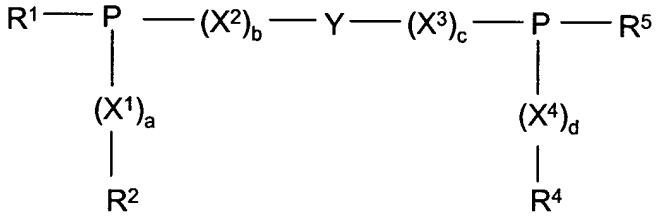
7. A process according to any of claims 2 to 6, wherein the fractionation of the output from the reaction in step b) comprises a thermal separation step and at least one high-boiling soluble base which is present in the catalytically active fluid after the fractionation is used.

8. A process according to any of claims 2 to 7, wherein at least one base immobilized on a solid phase is used and the catalytically active fluid obtained in step b) is brought into contact with the immobilized base before it is recirculated to the reaction zone.

9. A process according to any of the preceding claims, wherein the phosphoramidite compound is selected from among compounds of the formulae I and II



(I)



(II)

where

R^1 and R^5 are each, independently of one another, pyrrole groups bound via the nitrogen atom to the phosphorus atom,

R^2, R^3 and R^4 are each, independently of one another, alkyl, cycloalkyl, heterocycloalkyl, aryl or hetaryl,

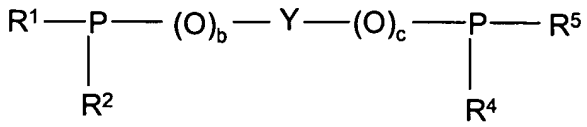
or R^1 together with R^2 and/or R^4 together with R^5 forms a divalent group containing at least one pyrrole group bound via the pyrrolic nitrogen atom to the phosphorus atom,

Y is a divalent bridged group having from 2 to 20 bridge atoms between the flanking bonds,

X^1, X^2, X^3 and X^4 are selected independently from among O, S, $SiR^{\alpha}R^{\beta}$ and NR^{γ}, where R^{α}, R^{β} and R^{γ} are each, independently of one another, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl or hetaryl, and

a, b, c and d are each, independently of one another, 0 or 1.

10. A process according to any of the preceding claims, wherein the phosphoramidite compound is selected from among compounds of the formula II.1

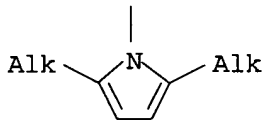


(II.1)

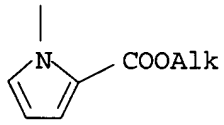
where

R^1, R^2, R^4, R^5, Y, b and c are as defined in claim 9.

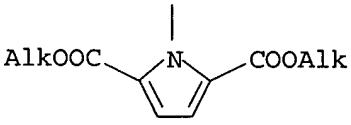
11. A process according to claim 9 or 10, wherein R^1, R^2, R^4 and R^5 are selected independently from among groups of the formulae III.a to III.k



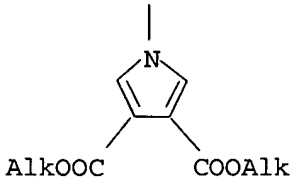
(III.a)



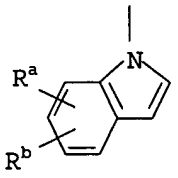
(III.b)



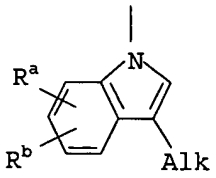
(III.c)



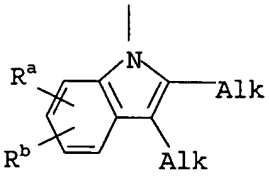
(III.d)



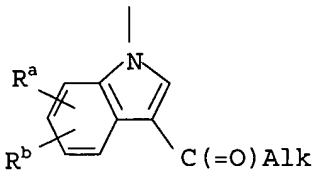
(III.e)



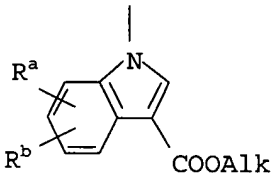
(III.f)



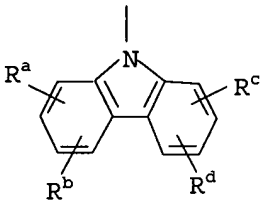
(III.g)



(III.h)



(III.i)



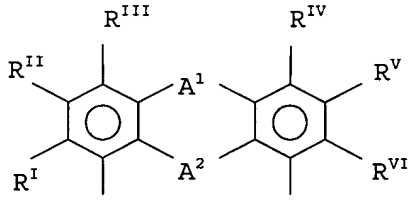
(III.k)

where

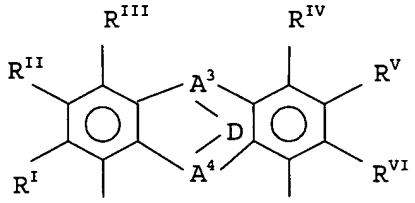
Alk is a C_1-C_{12}-alkyl group and

R^a, R^b, R^c and R^d are each, independently of one another, hydrogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, acyl, halogen, C_1-C_4-alkoxycarbonyl or carboxyl.

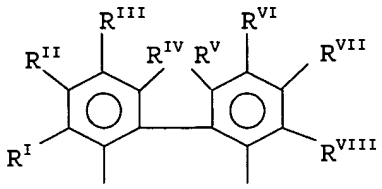
12. A process according to any of claims 9 to 11, wherein the bridging group Y is selected from among groups of the formulae IV.a to IV.u



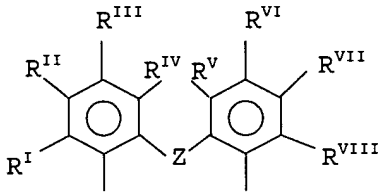
(IV.a)



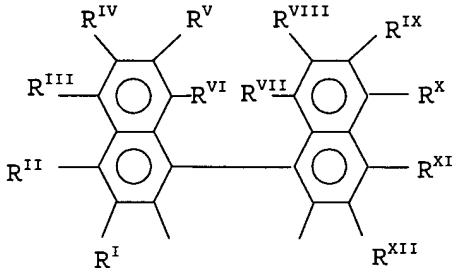
(IV.b)



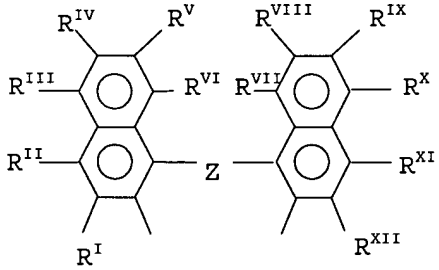
(IV.c)



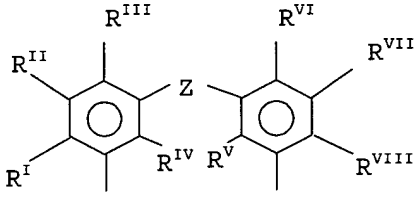
(IV.d)



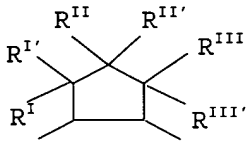
(IV.e)



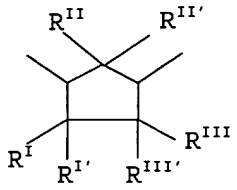
(IV.f)



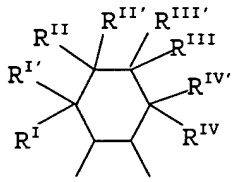
(IV.g)



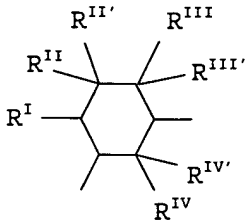
(IV.h)



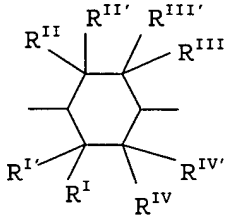
(IV.i)



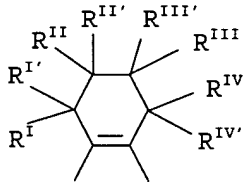
(IV.k)



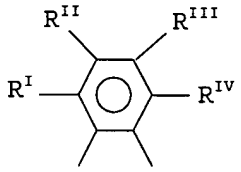
(IV.l)



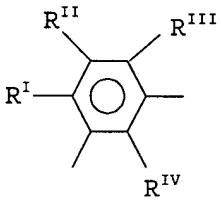
(IV.m)



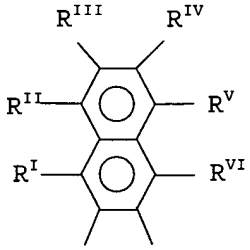
(IV.n)



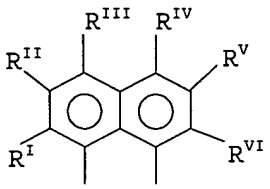
(IV.o)



(IV.p)

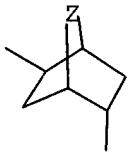


(IV.q)

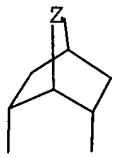


(IV.r)

(IV.s)



(IV.t)



(IV.u)

where

R^{I}, $R^{I'}$, R^{II}, $R^{II'}$, R^{III}, $R^{III'}$, R^{IV}, $R^{IV'}$, R^{V}, R^{VI}, R^{VII}, R^{VIII}, R^{IX}, R^{X}, R^{XI} and R^{XII} are each, independently of one another, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, hetaryl, hydroxy, thiol, polyalkylene oxide, polyalkylenimine, alkoxy, halogen, SO_3H, sulfonate, NE^1E^2, alkylene-NE^1E^2, nitro, alkoxycarbonyl,

carboxyl, acyl or cyano, where E^1 and E^2 are identical or different radicals selected from among hydrogen, alkyl, cycloalkyl and aryl,

Z is O, S, NR^δ or $SiR^\delta R^\varepsilon$, where
R^δ and R^ε are each, independently of one another, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl or hetaryl,

or Z is a C_1-C_4-alkylene bridge which may have a double bond and/or bear an alkyl, cycloalkyl, heterocycloalkyl, aryl or hetaryl substituent,

or Z is a C_2-C_4-alkylene bridge which is interrupted by O, S or NR^δ or $SiR^\delta R^\varepsilon$,

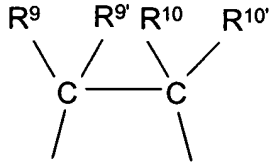
where, in the groups of the formulae IV.a and IV.b, two adjacent radicals R^I to R^{VI} together with the carbon atoms of the benzene ring to which they are bound may also form a fused ring system having 1, 2 or 3 further rings,

where, in the groups of the formulae IV.h to IV.n, two geminal radicals R^I, $R^{I'}$; R^{II}, $R^{II'}$; R^{III}, $R^{III'}$ and/or R^{IV}, $R^{IV'}$ may also represent oxo or a ketal thereof,

A^1 and A^2 are each, independently of one another, O, S, $SiR^\phi R^\gamma$, NR^η or $CR^\iota R^\kappa$, where R^ϕ, R^γ, R^η, R^ι and R^κ are each, independently of one another, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl or hetaryl,

A^3 and A^4 are each, independently of one another, SiR^ϕ, N or CR^ι,

D is a divalent bridging group of the formula



where

R^9, $R^{9'}$, R^{10} and $R^{10'}$ are each, independently of one another, hydrogen, alkyl, cycloalkyl, aryl, halogen, trifluoromethyl, carboxyl, carboxylate or cyano,

where $R^{9'}$ together with $R^{10'}$ can also represent the second bond of a double bond between the two carbon atoms to which $R^{9'}$ and $R^{10'}$ are bound, and/or R^9 and R^{10} together with the carbon atoms to which they are bound may also form a 4- to 8-membered carbocycle or heterocycle which may additionally be fused with one, two or three cycloalkyl, heterocycloalkyl, aryl or hetaryl groups, where the

heterocycle and, if present, the fused-on groups may each bear, independently of one another, one, two, three or four substituents selected from among alkyl, cycloalkyl, heterocycloalkyl, aryl, hetaryl, $COOR^f$, COO^-M^+, SO_3R^f, $SO^-_3M^+$, NE^4E^5, alkylene-NE^4E^5, $NE^4E^5E^{6+}X^-$, alkylene-$NE^4E^5E^{6+}X^-$, OR^f, SR^f, $(CHR^eCH_2O)_yR^f$, $(CH_2N(E^4))_yR^f$, $(CH_2CH_2N(E^4))_yR^f$, halogen, trifluoromethyl, nitro, acyl and cyano, where

R^f, E^4, E^5 and E^6 are identical or different radicals selected from among hydrogen, alkyl, cycloalkyl and aryl,

R^e is hydrogen, methyl or ethyl,

M^+ is a cation,

X^- is an anion and

y is an integer from 1 to 240.

13. A method of stabilizing a catalytically active fluid comprising a dissolved metal complex of a metal of transition group VIII of the Periodic Table of the Elements with at least one phosphoramidite compound as ligand in the hydroformylation of ethylenically unsaturated compounds, which comprises bringing the fluid into contact with a base.

14. A method according to claim 13, wherein the fluid is admixed with a base which is soluble therein and/or is brought into contact with a base immobilized on a solid phase.

15. The use of bases for stabilizing a catalytically active fluid comprising a dissolved metal complex of a metal of transition group VIII of the Periodic Table of the Elements with at least one phosphoramidite compound as ligand in the hydroformylation of ethylenically unsaturated compounds.